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(54) A process for the production of a hemicellulose hydrolysate and special pulp.

(57) The invention relates to a process for the production of a hemicellulose hydrolysate and special pulp through two steps, the first step comprising the prehydrolysis of the material and the second step the dissolving of the lignin contained in the prehydrolyzed material. According to the process the lignin dissolving is carried out by means of a neutral sulphite cooking with anthraquinone or a derivative thereof as a catalyst, the pH of the cooking liquor being initially at least 10.

DISSOLVING OF LIGNIN IN THE COOKING
STEPS OF THE DIFFERENT TESTS

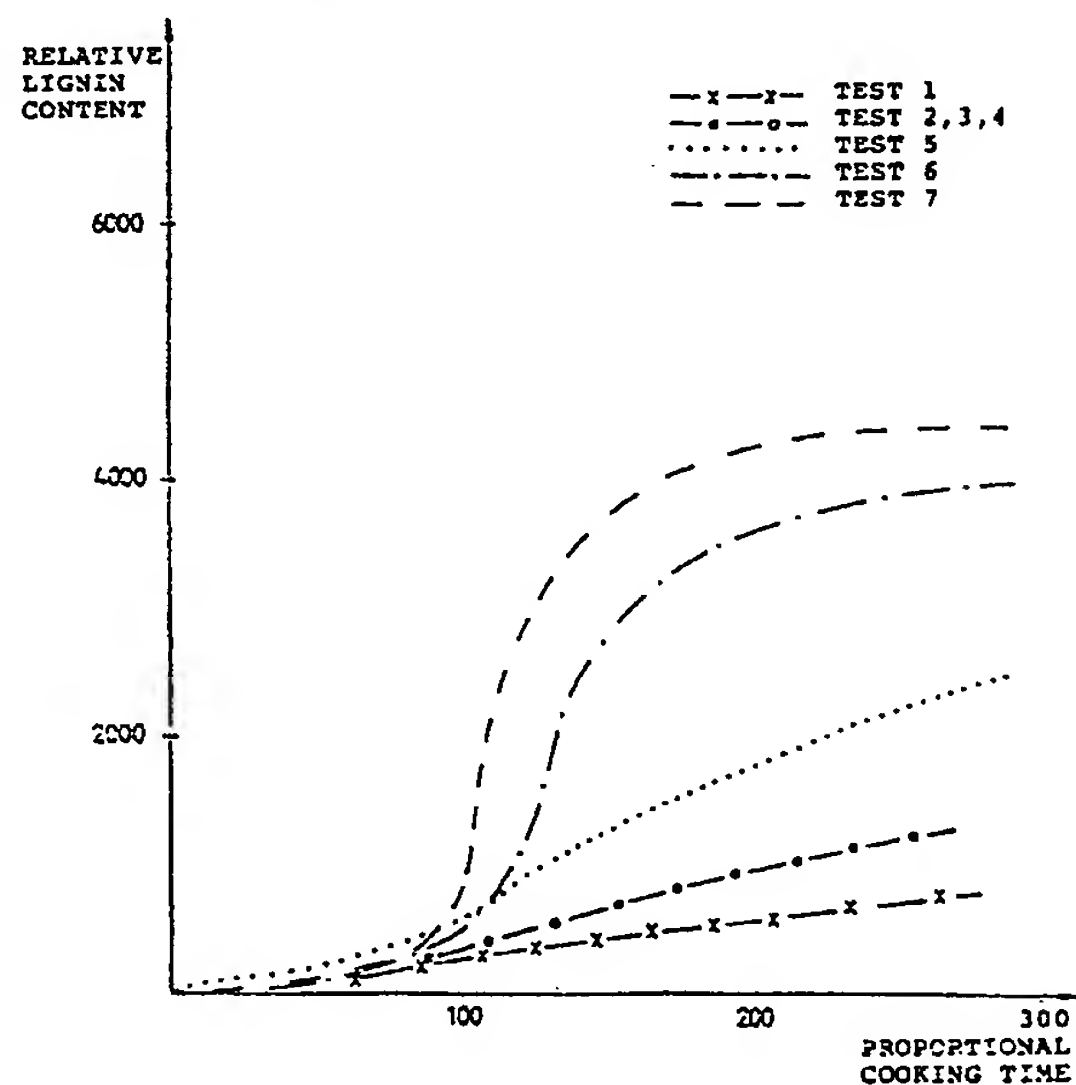


FIG. 1

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A process for the production of a hemicellulose hydrolysate and special pulp

The invention relates to a process for the production of a hemicellulose hydrolysate and special pulp from a material containing lignocellulose through two steps, the first step comprising the hydrolysis of hemicelluloses into simple sugars and the second step the dissolving of lignin for liberating cellulose fibres.

Traditionally, there are two processes for the production of special pulps having a high content of alpha cellulose, such as dissolving pulp: the faradvanced acidic bisulphite cooking and the prehydrolysis-sulphate cooking. The former was developed at the beginning of the 20th century and the latter in the 1930's, see e.g. Rydholm, S.E., *Pulping Processes*, p. 649 to 672, Interscience Publishers, New York, 1968. The basic idea in both processes is to remove as much hemicellulose as possible from cellulose fibres in connection with the delignification so as to obtain a high content of alpha cellulose. This is essential because the various uses of dissolving pulp, for instance, do not tolerate short-chained hemicellulose molecules with indefinite structure. In the sulphite process, the removal of hemicellulose takes place during the cooking simultaneously with the dissolving of lignin. The cooking conditions are highly acidic and the temperature varies from 140 to 150°C, whereby the hydrolysis is strong. The result, however, is always a compromise with delignification, and no high content of alpha cellulose is obtained. Another drawback is the decrease in the degree of polymerization of cellulose and the yield losses, which also limit the hydrolysis possibilities. Various improvements have been suggested in traditional sulphite cooking, the use of additional chemicals, for instance. Such additional chemicals, used in addition to the basic chemicals of sulphite cooking, include sulphide, white liquor, and anthraquinone, see e.g. Finnish Patent Specification 67 104 and U.S. Patent Specification 4 213 821. These sulphite cooking variations do not, however, imply hydrolytic conditions.

A separate prehydrolysis step is interesting in the view of the fact that it enables the adjustment of the hydrolysis of hemicelluloses as desired by varying the hydrolysis conditions. In the prehydrolysis-sulphate process the delignification is not carried out until in a separate second cooking step. The prehydrolysis is carried out either as a water prehydrolysis or in the presence of a catalyst. Organic acids liberated from wood in the water prehydrolysis perform a major part of the process, whereas small amounts of mineral acid or sulphur dioxide, in some cases even sulphite waste liquor, are added to the digester in "assisted"

prehydrolysis. It has previously been necessary to effect the lignin dissolving step after the prehydrolysis as sulphate cooking which has several drawbacks. The prehydrolysis-sulphate process has e.g. the following drawbacks:

-The yield is low because of the strong alkaline reaction conditions which cause splitting of cellulose. Thus the wood consumption per one ton of cellulose is high.

-The content of residual lignin is rather high because the step for the removal of residual lignin in the sulphate cooking process is extremely non-selective. Thus there is a great need of bleaching for complete removal of lignin, and the consumption of chemicals is high; further, at least five bleaching steps are required.

-Industrial realization of sulphate cooking is complicated, and the cost of investment very high.

Previously the use of sulphite cooking has not been possible, because it is not possible to dissolve from wood material lignin deactivated in the prehydrolysis by means of traditional sulphite cooking processes. It has been regarded as impossible to use a sulphite cooking step (cf. Rydholm above) even though it would have advantages over sulphate cooking.

It has now been found out unexpectedly that excellent results can be obtained by effecting the lignin dissolving after the prehydrolysis by an alkaline neutral sulphite cooking with anthraquinone or a derivative thereof as a catalyst. Such a cooking is known per se from the prior art (see e.g. U.S. Patent Specification 4 213 821); on the contrary, a combination of prehydrolysis and such a cooking has not been set forth previously.

The invention relates to a process for the production of hemicellulose hydrolysate and special pulp from a material containing lignocellulose through two steps, the first step comprising the prehydrolysis of the material and the second step dissolving of the lignin contained in the prehydrolyzed material. The process is characterized in that the dissolving of lignin is carried out by means of neutral sulphite cooking with anthraquinone or a derivative thereof as a catalyst, the pH of the cooking liquor being initially at least 10.

Suitable prehydrolyzing agents include e.g. water, mineral acid, sulphur dioxide, sulphite cooking acid, and sulphite waste liquor. Preferred prehydrolyzing agents include sulphur oxide, sulphuric acid, and water.

A suitable prehydrolyzing temperature is 100 to 180°C, preferably 155 to 170°C, and a suitable hydrolyzing time is 10 to 200 minutes, preferably 90 to 170 minutes.

The material containing lignocellulose preferably consists of softwood or hardwood.

The cooking step is suitably carried out with a cooking liquor comprising 100 to 400 g of sodium sulphite/kg of dry wood; 10 to 100 g of sodium carbonate/one kg of dry wood; sodium hydroxide for rising the pH of the cooking liquor to a value between 10 and 13; and 0.01 to 0.2%, calculated on dry wood, of anthraquinone or a derivative thereof.

The cooking temperature preferably ranges from 160 to 180°C, and the cooking time is suitably 100 to 200 minutes after the temperature has risen 0.1 to 2°C/min from a temperature varying between room temperature and 100°C.

It is typical of the prehydrolysis-neutral sulphite-anthraquinone process (PH-NS-AQ process) that delignification to a low content of residual lignin is easy to carry out while the yield of cellulose fibre, however, remains on an exceptionally high level. Thus it is possible to use strong prehydrolysis conditions (e.g. strong acids, such as H₂SO₄), whereby the hydrolysis of hemicelluloses into simple sugars is efficient; on the other hand, the alpha cellulose content representing the content of residual hemicellulose in cellulose fibre is high and the content of residual pentosan is low. Due to these properties the process is particularly suitable for the production of highquality dissolving pulp, for instance, whereby monosaccharides are obtained simultaneously.

As to the new process, it was found out that the use of the so called neutral sulphite anthraquinone cooking process effects a partial ionization of the lignin inactivated in the prehydrolysis, the initial pH being at least 10, e.g. 11 to 12, and that anthraquinone as an additive in the cooking catalyzes the breaking of nucleophilic beta aryl ether bonds, which at the end results in the liberation of fibres, i.e. a successful cooking. It was further found out that sulphite ions in neutral sulphite cooking react simultaneously and participate in the decomposing of the structure of lignin and above all sulphonate the lignin material and fragments which thus become more hydrophilic and dissolve more easily in the cooking liquor, thus contributing to the formation of a successful cooking and to the continuation thereof to a very low content of residual lignin. In short, the prehydrolysis-neutral sulphite anthraquinone process according to the invention not only gives a result as successful as that of the sulphate process but also provides all the advantages typical of sulphite cooking.

The increased yield of the process according to the invention is due to the fact that there does not occur splitting of cellulose to any greater degree during the neutral sulphite cooking step. In sulphate cooking, on the contrary, the high alkalinity

causes alkaline hydrolysis, and the peeling-off reaction in particular results irrevocably in a yield loss. The process according to the invention enables the recovery of nearly all of the high molecular weight cellulose material originally contained in the wood material.

In the process-chemical sense, another advantage is that pulp which has undergone neutral sulphite anthraquinone cooking is easy to bleach, i.e. the residual lignin remaining in the fibre after the cooking is easy to remove. This is due to the fact that the delignification resembles sulphite cooking; the condensation of the structure of lignin is insignificant; and the sulphonation makes lignin more hydrophilic. Contrary to this, the residual lignin in sulphate cooking is strongly condensed and the content thereof is on a higher level. The removal of this kind of residual lignin in bleaching requires five to six bleaching steps and plenty of expensive chlorine dioxide. The bleaching of pulp obtained by means of the process according to the invention can be carried out by three steps only and the demand of chemicals, too, is lower.

The process according to the invention has the following advantages:

-The yield of the special pulp to be produced in connection with the production of sugars is increased, which improves the production economy.

-The process after the prehydrolysis is simplified, which decreases the cost of investment.

-The easier delignification in the cooking step decreases the need of bleaching, thus improving the production economy and reducing the emission of chlorinated compounds from the bleaching.

-The oxygen or peroxide step after the cooking is extremely efficient as compared with that of the prehydrolysis-sulphate process, whereby the recovery and economy are improved.

-Small-scale production is economically more interesting because it is possible to operate in connection with an existing sodium-based sulphite pulp mill without any appreciable additional investments.

The following examples are illustrative of the invention.

The following abbreviations are used in the examples:

Steps of the bleaching processes

O = Oxygen step

D = Chlorine dioxide step

E = Alkali extraction

P = Peroxide step

H = Hypochlorite step

C = Chlorination

Standards

SCAN = Scandinavian standard

TAPPI = U.S. standard

Example 1Production of a birch hydrolysate and special pulp by means of the PH-NS-AQ process from birch chips

Chips and a prehydrolyzing liquor were metered into a chip basket positioned in a 20-litre forced circulation digester. The cover of the digester was closed and the prehydrolysis was carried out according to the temperature program by heating the digester circulation indirectly by means of steam. After the hydrolysis time had passed, the hydrolysate was removed from the digester and recovered. The prehydrolyzed chip material contained in the digester was washed in the digester for 5 minutes with warm water, the cover was opened, and the chips were passed into a centrifuge in which excess water was removed. The centrifugalized material was weighed and a dry substance sample was taken for determining the hydrolysis loss.

The prehydrolyzed chip material was returned to the digester, cooking liquor and anthraquinone were added, the cover was closed, and the cooking was carried out according to the temperature program. At the end of the cooking the cooking liquor was removed rapidly and the digester was filled with cold water, whereafter water was allowed to flow for 10 hours for washing the cooked chip material. After the wash the pulp was disintegrated by means of a wet disintegrator for one minute and assorted with a flat screen plate of 0.35 mm. Shives were recovered and weighed dry for determining the shive content. The accepted fraction was passed into the centrifuge for dewatering, homogenized, and weighed. Laboratory analyses were carried out on this pulp and the pulp was further used in bleaching tests.

Prehydrolyzing step

Wood amount, g of abs. dry chips 2000

Prehydrolyzing agent SO₂

Amount of prehydrolyzing agent, % on dry wood 0.25

Liquor ratio 6:1

Temperature rising time, min 40

Prehydrolysis temperature, °C 155
Prehydrolysis time, min 170
Prehydrolysis loss, % on wood 26.6

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Cooking stepNa₂SO₃, % on wood as NaOH 22Na₂CO₃, % on wood as NaOH 5

Anthraquinone, % on wood 0.1

10 Liquor ratio 4.5:1

pH of the cooking liquor 11.3

Rising of the temperature °C/min 1

Cooking temperature, °C 175

Cooking time, min 170

15 Yield, % on wood 39.3Kappa number 17.2

Shive content, % on wood 0.1

Properties of O-D-E-D bleached pulp

Final yield, % of wood 36.7

20 ISO brightness 87.1

Alpha cellulose % 94.2

Viscosity, SCAN dm³/kg 76425 Example 2Production of a birch hydrolysate and special pulp by the PH-NS-AQ process from birch chips

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The test was carried out as dislocated in Example 1.

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Prehydrolyzing step

Wood amount, g of abs. dry chips 2500

Prehydrolyzing agent SO₂

Amount of prehydrolyzing agent,

40 % on dry wood (SO₂) 0.25

Liquor ratio 3.5:1

Temperature rising time, min 40

Prehydrolysis temperature, °C 155

Prehydrolysis time, min 170

45

Cooking stepNa₂SO₃, % on wood as NaOH 20Na₂CO₃, % on wood as NaOH 6

50 Anthraquinone, % on wood 0.1

Liquor ratio 4.5:1

pH of the cooking liquor 11.3

Rising of the temperature °C/min 1

Cooking temperature, °C 175

55 Cooking time, min 170

Yield, % on wood 46.7Kappa number 48.1

Shive content, % on wood 1.35

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Properties of O-P-H bleached pulp
 Final yield, % on wood 39.7
 ISO brightness 87.1
 Alpha cellulose % 91.7
 Viscosity, SCAN dm³·kg 530

Example 3

Production of a birch hydrolysate and special pulp by the PH-NS-AQ process from birch chips

The test was carried out as disclosed in Example 1.

Prehydrolyzing step

Wood amount, g of abs. dry chips 2500
 Prehydrolyzing agent H₂SO₄
 Amount of prehydrolyzing agent, % on dry wood 1.0
 Liquor ratio 3.5:1
 Temperature rising time, min 40
 Prehydrolysis temperature, °C 155
 Prehydrolysis time, min 90
Prehydrolysis loss, % on wood 25.4

Cooking step

Na₂SO₃, % on wood as NaOH 22
 Na₂CO₃, % on wood as NaOH 5
 Anthraquinone, % on wood 0.1
 Liquor ratio 4.5:1
 pH of the cooking liquor 11.3
 Rising of the temperature °C/min 1
 Cooking temperature, °C 175
 Cooking time, min 170
Yield, % on wood 37.0
Kappa number 24.9
 Shive content, % on wood 0.6
 Properties of C-E-D bleached pulp
 Final yield, % on wood 34.2
 ISO brightness 90.0
 Alpha cellulose % 94.6
 Viscosity, SCAN dm³·kg 730
 Properties of O-P-D bleached pulp
 Final yield, % on wood 34.7
 ISO brightness 84.4
 Alpha cellulose % 94.5
 Viscosity, SCAN dm³·kg 720

Example 4

Production of a pine hydrolysate and special pulp by the PH-NS-AQ process from pine chips

5 The test was carried out as disclosed in Example 1.

Prehydrolyzing step

10 Wood amount, g of abs. dry wood 2000
 Prehydrolyzing agent H₂O
 Liquor ratio 6:1
 Temperature rising time, min 45
 Prehydrolysis temperature, °C 170
 15 Prehydrolysis time, min 15
Prehydrolysis loss, % on wood 13.2

Cooking step

20 Na₂SO₃, % on wood as NaOH 22
 Na₂CO₃, % on wood as NaOH 5
 Anthraquinone, % on wood 0.2
 Liquor ratio 4.5:1
 pH of the cooking liquor 11.3
 25 Rising of the temperature °C/min 1
 Cooking temperature, °C 175
 Cooking time, min 170
Yield, % on wood 40.3
Kappa number 16.5
 30 Shive content, % on wood 0.4
 Properties of O-D-E-D bleached pulp
 Final yield, % on wood 37.2
 ISO brightness 84.2
 Viscosity, SCAN dm³·kg 890

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Reference example

40 It was studied how lignin dissolves in cooking processes generally in use as compared with the cooking step of the process according to the invention when the chips are prehydrolyzed according to the prior art. Sulphate cooking and various modifications of sulphite cooking are processes in general use.

45 In the tests the prehydrolysis/cooking was carried out as follows:

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Test 1

55 Sulphur dioxide water prehydrolysis, normal
 Normal acidic Ca bisulphite cooking step
 Kappa number 150

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Test 2

Sulphur dioxide water prehydrolysis, normal
Normal acidic Ca bisulphite cooking step
Kappa number 126

Test 3

Water prehydrolysis, weak
Normal acidic Ca bisulphite cooking step
Kappa number 118

Test 4

Sulphur dioxide water prehydrolysis, weak
Neutralizing lime milk treatment
Acidic Ca bisulphite cooking step with an extremely
high bound SO₂
Kappa number 106

Test 5

Sulphur dioxide prehydrolysis
Cooking step 1: ammonium neutral sulphite cooking
Cooking step 2: sulphur dioxide water acidic sulphite cooking
Kappa number 141

Test 6

Sulphur dioxide water prehydrolysis, normal
Neutral sulphite-anthraquinone cooking step
Kappa number 48

Test 7

Sulphur dioxide water-prehydrolysis, normal
Sulphate cooking step, normal
Kappa number 14

Lignin concentrations measured from the digester during the cooking step by means of a cooking liquor analyzer as a function of the cooking time reduced to the same scale appear from the attached figure 1. The curves thus illustrate the dissolving of lignin as measured as an increase in the lignin content of the cooking liquor. The results show that the cooking step after the prehydrolysis in Tests 1 to 4 does not dissolve lignin efficiently even though attempts have been made to improve these sulphite processes as much as possible. The dissolving obtained in Test 5 was better because the prehydrolysis is exceptional and not technically reasonable. The content of residual lignin in Test 5 (the kappa number exceeding 100) is, however, technically impossible, the reasonable level being the kappa number of about 50 (= about 10% of lignin in cooked pulp). In Tests 6 and 7, lignin

starts to dissolve rapidly in the relative cooking time of 100, the subsequent step being the main delignification of a successful cooking which is completed by a slow residual delignification towards the end of the cooking. In this way, the kappa level of 40 in Test 6 and the kappa level of 15 in Test 7 were achieved. Accordingly, it is obvious that an efficient removal of lignin from prehydrolyzed chip material takes place in the cooking step of the process according to the invention such as disclosed in Test 6; thus, it can replace the sulphate cooking used in Test 7.

The tests carried out show that normal technical prehydrolysis conditions inactivate lignin to such an extent that no cooking modification within an acidic or neutral cooking pH range is able to dissolve lignin even though the chip material would be neutralized between the prehydrolysis and the cooking. The sulphite cooking step used in the process according to the invention is operative only when the cooking conditions and the cooking catalyst are chosen appropriately.

Claims

1. A process for the production of a hemicellulose hydrolysate and special pulp from a material containing lignocellulose through two steps, the first step comprising the prehydrolysis of the material and the second step the dissolving of the lignin contained in the prehydrolyzed material, **characterized** in that the dissolving of lignin is carried out by means of a neutral sulphite cooking with anthraquinone or a derivative thereof as a catalyst, the pH of the cooking liquor being initially at least 10.

2. A process according to claim 1, **characterized** in that the material containing lignocellulose is hardwood.

3. A process according to claim 1, **characterized** in that the material containing lignocellulose is softwood.

4. A process according to any of the preceding claims, **characterized** in that the prehydrolysis is carried out by means of water, sulphur dioxide or sulphuric acid at a temperature of 155 to 170°C for 90 to 170 minutes.

5. A process according to any of the preceding claims, **characterized** in that the cooking is carried out by means of a cooking liquor comprising 100 to 400 g of sodium sulphite/kg of dry wood; 10 to 100 g of sodium carbonate/kg of dry wood; sodium hydroxide for rising the pH of the cooking liquor to a value varying from 10 to 13; and 0.01 to 0.2% (calculated on dry wood) of anthraquinone or a derivative thereof, at a temperature of 160 to

180°C for 100 to 200 minutes after the temperature is raised 0.1 to 2°C/min from a temperature varying between room temperature and 100°C.

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DISSOLVING OF LIGNIN IN THE COOKING
STEPS OF THE DIFFERENT TESTS

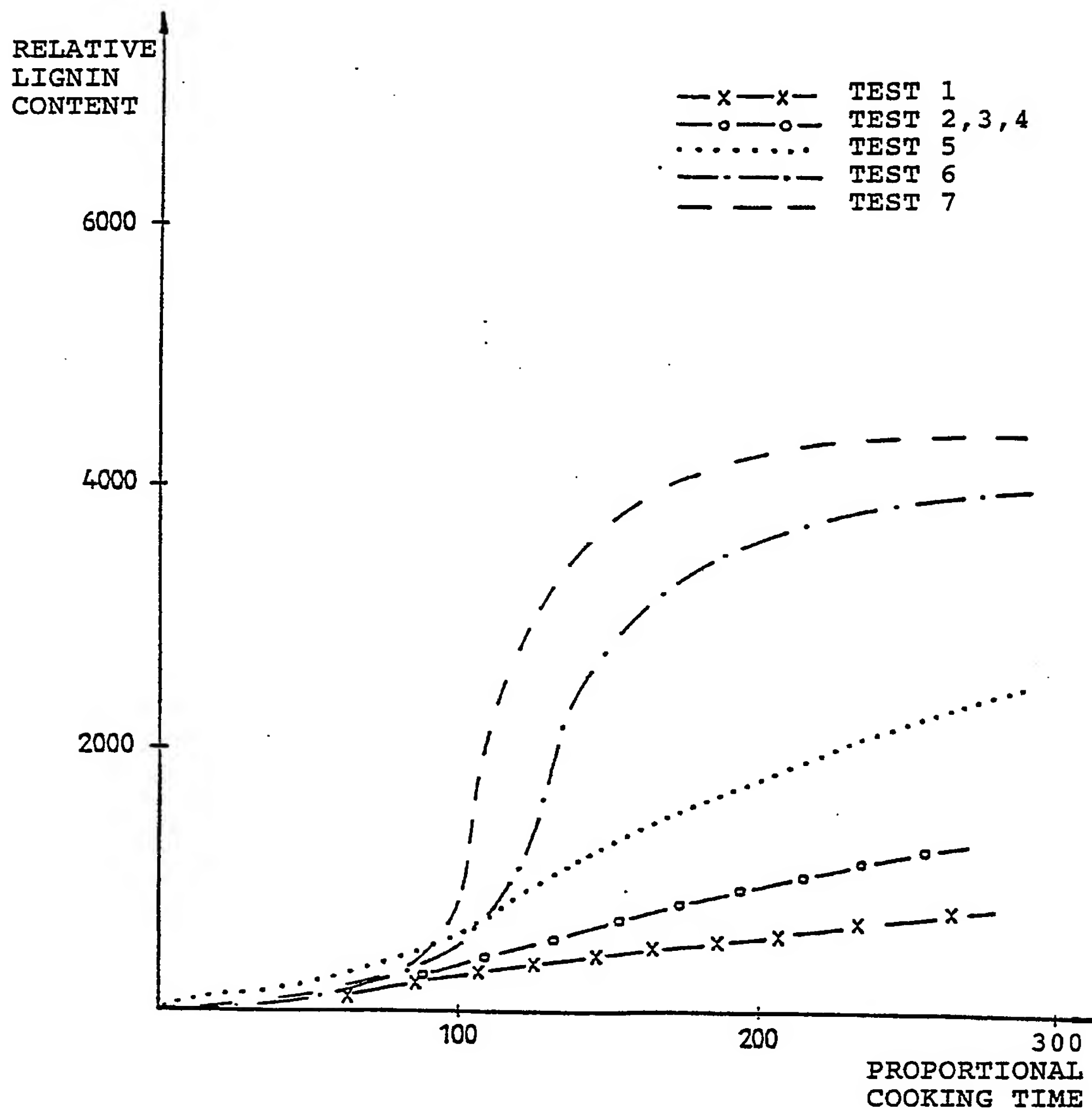


FIG. 1

For the purpose of publication, correction(s)

☐ allowed

☐ allowed with exception of the deleted points

☐ not allowed

Signature: _____ date: _____

Receiving Section